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# Structural Changes during the Decomposition of Calcium Hydroxide

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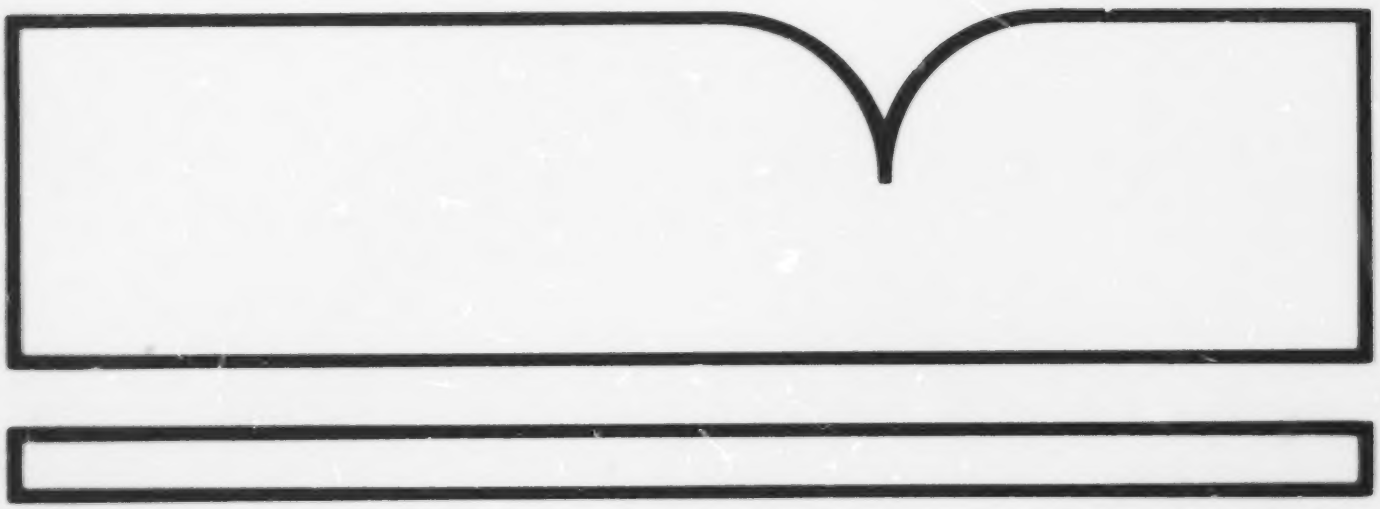

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16. ABSTRACT The paper discusses the production of calcium hydroxides with surface areas of 6-74 sq m/g, in an attempt to develop more reactive sorbents for SO2 capture during furnace injection. It was found that adding alcohol to the water of hydration yielded hydroxides with surface areas up to 40 sq m/g. The sorbents were produced using "double hydration" and a mixture of water and methyl alcohol. When these sorbents were injected into the boiler, however, only marginal increases in SO2 capture were observed. The purpose of this research was to monitor structural changes in these sorbents during calcination in order to determine the reason for their relatively poor performance. For a given calcine and fixed conditions of calcination, the surface area decreased and median pore size increased with decreasing particle size in the 1.2-7.5 micrometer size range. This suggests that sintering advances more quickly in fine particles. For sorbents described here and using one precursor limestone, a correlation could be found between structural properties of Ca(OH)2 and nascent CaO. Increased surface area of Ca(OH)2 led to higher surface area of CaO after calcination at fixed conditions. The theoretical existence of an optimum combination of surface area and porosity of CaO was verified.

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# STRUCTURAL CHANGES DURING THE DECOMPOSITION OF CALCIUM HYDROXIDE

by:

Wojciech Jozewicz
Acurex Corporation
Environmental Systems Division
Post Office Box 13109
Research Triangle Park, North Carolina 27709

and

David A. Kirchgessner and Brian K. Gullett
U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, North Carolina 27711

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# STRUCTURAL CHANGES DURING THE DECOMPOSITION OF CALCIUM HYDROXIDE

WOJCIECH JOZEWICZ
Acurex Corporation
Environmental Systems Division
Post Office Box 13109
Research Triangle Park, North Carolina 27709

DAVID A. KIRCHGESSNER AND BRIAN K. GULLETT
U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, North Carolina 27711

## ABSTRACT

In an attempt to develop more reactive sorbents for sulfur dioxide ($SO_2$) capture during furnace injection, calcium hydroxides with surface areas of 6 to 74 $m^2/g$ were produced. It was found that adding alcohol to the water of hydration yielded hydroxides with surface areas up to 40 $m^2/g$. Sorbents with surface areas up to 74 $m^2/g$ were produced using a "double hydration" method and a mixture of water and methyl alcohol. When these sorbents were injected into the boiler, however, only marginal increases in $SO_2$ capture were observed. The purpose of this research was to monitor structural changes in these sorbents during calcination in order to determine the reason for their relatively poor performance.

Sorbents were calcined in an isothermal differential flow reactor operated within a 550 to 1000 °C temperature range. Sorbents with specific surface areas of 6 to 74 $m^2/g$ were used. Specific surface area, porosity, and pore size distribution of calcined sorbents were monitored.

A high temperature inertial cascade impactor was used to collect size cuts for measurement of structural properties of calcines as a function of their particle sizes. For a given calcine and fixed conditions of calcination, the surface area decreased and median pore size increased with decreasing particle size in the 1.2 to 7.5 μm size range. This suggests that sintering advances more quickly in fine particles.

For sorbents described here and using one precursor limestone, a correlation could be found between structural properties of calcium hydroxide [$Ca(OH)_2$] and nascent calcium oxide (CaO). Increased surface area of $Ca(OH)_2$ led to higher surface area of CaO after calcination at fixed conditions. The theoretical existence of an optimum combination of surface area and porosity of CaO for reactivity with $SO_2$ was verified in the short time differential reactor.

## INTRODUCTION

The limestone injection multistage burner (LIMB) process is a low capital cost, dry sorbent injection technology developed by the U.S. Environmental Protection Agency. The cost of the $Ca(OH)_2$ sorbent injected into the furnace constitutes a significant part of the overall operating expenses, therefore it is important to ensure reasonable sorbent utilization. Upon furnace injection the sorbent decomposes to CaO, which reacts with $SO_2$, and sinters. Since CaO is the species which reacts with $SO_2$, most research has been directed to understanding how properties of CaO can affect the reaction. Numerous studies have elucidated the ability of smaller particle size to increase the reactivity of sorbents [1,2,3,]. It is also known that, generally, the size distribution of CaO is similar to that of the parent $Ca(OH)_2$ [4]. Surface area, porosity, and pore structure of CaO have been recognized as having a major effect upon reactivity with $SO_2$. Higher reactivity with $SO_2$ for sorbents with higher calcined surface areas has been documented by several authors [5,6,7]. Reactivity has been found to increase with the square of the BET surface area of the CaO [8]. The role of porosity has been discussed [9], and the importance of pore size distribution in minimizing the resistance to the diffusing species has been recognized [10]. Research examining the combined effect of particle size, porosity, and surface area of the sorbent reacting with $SO_2$ has been conducted and suggests that a combination of surface area in the range 30 to 50 $m^2/g$ and porosity in the range 0.3 to 0.4 could be optimal for $SO_2$ capture [11].

Detailed research has also been conducted to better understand the process of sintering of nascent CaO, which occurs simultaneously with the reaction with $SO_2$. It has been demonstrated that the process is governed by lattice diffusion [12] and is catalyzed by carbon dioxide and water present in the gas phase [13]. The initial effect of sintering upon the structure of the sorbent is to significantly reduce surface area while effecting only slight declines in pore volume and porosity [14]. Sorbents have been developed [15,16] that possess increased resistance to sintering and enhanced $SO_2$ capture upon furnace injection [17]. It has also been demonstrated that small amounts of $SO_2$ (below 50 ppm) present during calcination of $Ca(OH)_2$ increase the surface area of CaO compared to calcination without $SO_2$ [18,19].

Several attempts have been made to correlate the reactivity of CaO with $SO_2$ with properties of the precursor $Ca(OH)_2$. A broad study was conducted [20] comparing a variety of $Ca(OH)_2$ sources to their reactivity with $SO_2$. Relatively narrow utilization ranges were observed for the investigated sorbents. However, the potential for economic benefit dictates the need for reevaluation of potential correlations between structural properties of $Ca(OH)_2$ with properties of CaO and, ultimately, CaO's reactivity with $SO_2$. The latter step is rather well documented as discussed above.

The objective of this work is to determine if the structural properties of CaO can be correlated with those of the parent $Ca(OH)_2$. Another objective is to explain why some sorbents with extremely high specific surface areas [such as alcohol-modified $Ca(OH)_2$] are not significantly more reactive with $SO_2$. Two simplifications were made during this study. Only one precursor, calcium carbonate ($CaCO_3$), was used to produce sorbents with a wide range of surface area/porosity. Secondly, no chemical additives were used during hydration which would leave residues in the $Ca(OH)_2$. Methyl alcohol used for the enhancement of surface area in $Ca(OH)_2$ is believed to have evaporated completely by the time hydration is complete. The resulting sorbent does not contain impurities that could affect its pore structure during sintering/reaction with $SO_2$.

## EXPERIMENTAL

### Materials and Hydration

Limestone was obtained from the Longview Lime Division of the Dravo Lime Company in Saginaw, Alabama. It was crushed to a $D_{50}$ of 7.6 μm and calcined to CaO at 1,000 °C for 16 h in a Lindberg furnace under a nitrogen flow of 6 L/min. Hydration was conducted in a laboratory-scale hydrator consisting of a 0.4 L Pyrex beaker suspended in a constant 100 °C bath. A mechanically propelled stirrer was used to mix the water and lime. Each hydration was conducted by loading 10 g of dry lime into the hydrator and allowing the lime to achieve thermal equilibrium in the bath. The stirrer was started, and a single rapid addition of water was syringed into the hydrator in the desired molar ratio of $H_2O/CaO$. After 15 min, the hydration vessel was purged of remaining water vapor with nitrogen, leaving a thoroughly dry product. Modified hydrates were produced by adding a sufficient amount of alcohol to the hydration water to produce the desired ratio of alcohol to water.

A "double hydration" method was used to produce $Ca(OH)_2$ with specific surface areas in excess of 40 $m^2/g$. This method is known [21] to yield hydrated lime with extremely high reactivity. In the first step, regular hydrate was produced by the addition of water in the molar ratio of $H_2O/CaO = 2.6$. Next, this $Ca(OH)_2$ was calcined to CaO at 500 to 600 °C for 16 h in a Lindberg furnace under a nitrogen flow of 6 L/min. $Ca(OH)_2$ calcined in this way was 10 to 20 percent $Ca(OH)_2$ and upon hydration with a water/alcohol mixture yielded a "double hydrate" with a specific surface area of up to 74 $m^2/g$. The specific surface area of a double hydrate was a function of calcination temperature and the alcohol/water ratio during the second hydration.

### Reactors

The electrically heated, isothermal flow reactor into which the hydrates were injected for structural studies is shown in Figure 1. The reaction chamber consists of two concentric, 3.35 m long quartz tubes heated by three Lindberg tube furnaces. The inner tube has a 15 mm ID, and the outer tube has a 50.8 mm OD. Premixed gases enter the reactor at the bottom of the annulus between the inner and outer tubes and are heated as they move upward. At the top of the reactor they enter the inner tube with the sorbent and move downward through the reaction zone. Gases and solids exit the reactor through an air-cooled heat exchanger that quenches the reactant stream to approximately 280 °C. Solids are captured in a cyclone. Sorbent was fed from a fluidized bed feed tube through 1.9 mm ID syringe tubing. For this work the reactor was operated at nominal temperatures of 550 to 1,000 °C, and a nominal residence time of 1 s. Gas composition was 95 vol percent $N_2$, and 5 vol percent $O_2$ to be compatible with earlier experiments. $SO_2$ was omitted in this case because the objective of the research was to observe calcination and sintering behavior without the additional complication of sulfation, which would effectively mask the surface area and pore structure changes of interest through product layer buildup and pore plugging.

A short time differential reactor (STDR) was used for reactivity measurements. It is a fixed bed in which sorbent dispersed on a quartz wool is rapidly moved into the process gas stream and then extracted after a preset exposure time. The STDR apparatus shown in Figure 2 is centered around a pneumatically actuated sample slider assembly. The slider assembly is made of polytetrafluoroethylene (PTFE). This construction allows an inert carrier for the sample. To activate the slider assembly the start button is pushed, which simultaneously activates the 4-way valve and starts the timer. The valve then allows the compressed gas [630 kPa ($kN/m^2$)] to move the sample slider assembly. This results in positioning the sample bed holder under the reactive process gas. The valve reverses the flow of gas and drives the piston and connected sample slider assembly after the preset time expires. The sorbent sample is supported by a wire mesh, which holds a thin bed of quartz wool containing the dispersed sorbent. The sample slider is constructed in such a way as to allow for an uninterrupted gas flow. This prevents a sudden pressure buildup while sliding the sample bed from the nitrogen flow to the reactive gas flow. More details and operational characteristics are available elsewhere [22].

### Analyses

Specific surface area, porosity, and pore size distribution are measured by $N_2$ adsorption/desorption in a Micromeritics Digisorb 2400 autoanalyzer. Machine error is less than ±1 percent. Calcium utilization or conversion of reactor products is calculated after analyses for calcium by atomic absorption spectrophotometry and for sulfate by ion chromatography. Calcium utilization analyses have a precision of ±5 percent. The degree of hydration and extent of calcination are measured using a Perkin Elmer TGA7 thermogravimetric analyzer. Aerodynamic particle size analyses are performed by passing the particle-laden gases exiting the reactor through a heated Gelman cascade inertial impactor (Gelman particle sizing stack sampler no. 4024-29). This particular impactor is used because of its ability to withstand temperatures up to 800 °C. The median diameter range of particles that can be classified is 0.44 to 7.55 μm in increments of seven trays. A preimpactor collects all particles larger than 11.9 μm.

## RESULTS AND DISCUSSION

### Calcium Hydroxide

A wide range of sorbents representing varying combinations of specific surface area and porosity were necessary to study the relation between structural properties of $Ca(OH)_2$ and the CaO resulting from thermal decomposition. Several methods of producing high surface area $Ca(OH)_2$ were precluded from use throughout this study. Sodium salts and sugar are known to produce high surface areas; however, the residue of these additives in the sorbent could potentially alter the sintering behavior of $Ca(OH)_2$.

One method employing an additive during hydration of CaO and resulting in chemically pure $Ca(OH)_2$ is the use of alcohol. Alcohol evaporates as a result of heat produced from the exothermic reaction of CaO and $H_2O$, and in doing so removes most of the evolving heat of hydration. The population of hydrates produced for the purpose of this study is presented in Figure 3. Specific surface area of the hydrates is presented there as a function of porosity. Three classes of hydrates are plotted in Figure 3: hydrates without alcohol, hydrates with alcohol, and double hydrates with alcohol. A wide variety of hydration temperature, ratio of water/alcohol, and excess over stoichiometric demand for the water of hydration were used in the group of hydrates with alcohol. The resulting specific surface areas and porosities reached maximums of about 40 $m^2/g$ and 0.25, respectively. Double hydrates with alcohol yielded $Ca(OH)_2$ with surface areas above 70 $m^2/g$ and close to 0.5 porosity. This was in marked contrast to double hydrates without alcohol which yielded only 25 $m^2/g$ surface area and 0.2 porosity. A reasonable correlation could be found between specific surface area and porosity of sorbents produced throughout this study. All the sorbents presented in Figure 3 were produced from the Longview calcium carbonate precursor.

In an effort to better understand how the specific surface area of $Ca(OH)_2$ is created, the pore size distribution of several sorbents with dissimilar surface areas was measured. Figure 4 presents the results of pore size distribution analyses for $Ca(OH)_2$ of varying specific surface areas and porosities. The increase of sorbent surface area from 25 to 52 $m^2/g$ was achieved by increased pore volume in pores ranging in size from 30 to 1,000 Å. No significant increase of pore volume for pores smaller than 100 Å could be detected for $Ca(OH)_2$ with 74 $m^2/g$ compared to $Ca(OH)_2$ with 52 $m^2/g$. In this case the majority of pore volume increase took place in pores several hundred angstroms in diameter.

### Calcium Hydroxide-Calcium Oxide

Structural properties of $Ca(OH)_2$ such as specific surface area, porosity, and pore size distribution are very informative about the extent of hydration. However, the reactive form of sorbent is CaO and its properties directly affect reactivity with $SO_2$. Therefore, it would be very desirable to know any existing correlation between structural properties of CaO and its parent $Ca(OH)_2$. In order to find such correlations, sorbents produced in the bench-scale hydrator were extensively characterized using nitrogen adsorption. To accomplish this, sorbents were calcined in the flow reactor operated under fixed conditions of temperature and residence time. Conditions were selected that would allow the production of calcines in an early stage of sintering.

Previous work [15,16,18] indicates that for $Ca(OH)_2$ such conditions could be attained at temperatures slightly above the decomposition temperature of $Ca(OH)_2$ (typically 450 to 500 °C) and short residence time. Sorbents that are in the early stage of sintering are known to have constant porosity and changing surface area as a result of the growth of necks between adjacent particles or grains. As a result of neck growth, the rounding of pores located at the intersection of grain boundaries occurs. For this reason 550 °C and 1 s of residence time were selected as calcination conditions in the flow reactor. Sorbents were fed from the vibration-activated fluidized bed feeder and, after passing through the flow reactor, were separated from the gas by a cyclone. Following collection in the cyclone, solids were immediately transferred to a sample vial, sealed, and placed in a vacuum desiccator to await same-day structural analysis. These precautions were taken to minimize possible rehydration or recarbonation of calcines.

The results of this investigation are presented in Figures 5 and 6. Figure 5 shows the correlation between the specific surface area of calcium oxide [$S_A$-CaO] and the specific surface area of parent calcium hydroxide [$S_A$-$Ca(OH)_2$]. The corresponding correlation for porosity is given in Figure 6. A considerably better correlation for porosities could be found than for specific surface areas. This was probably the result of flow reactor conditions selected for calcination (550 °C,1 s). Under these conditions, sorbents should be only mildly sintered. This initial stage of sintering is characterized by a rapid deterioration of specific surface area and almost constant porosity, which undergoes changes only during more advanced stages of sintering. It is conceivable, therefore, that a small variability in calcination conditions such as local heat transfer parameters due to the varying particle size, or pulsations in the feed rate of sorbent into the flow reactor as a result of agglomeration in the feeder could exert a considerable effect on the fragile structure of CaO in the early stage of sintering. Significantly larger variability in process conditions than that typical for the operation of the flow reactor would have to occur to introduce significant scatter into porosity data. It should be pointed out, however, that the data presented in Figures 5 and 6 were acquired for one parent stone (Longview calcium carbonate). No such correlation was possible throughout the broader study [20] investigating commercial $Ca(OH)_2$ from several sources. It is believed that varying amounts of impurities, as well as different conditions of hydration, were responsible for the scatter in that data.

The mechanism of the decay of structural properties of nascent CaO upon sintering in the controlled environment of the flow reactor was next examined in greater detail. Sorbents that were produced in the bench scale hydrator were divided into three groups, according to their surface area. The low, intermediate, and high surface area ranges were selected to be below 30 $m^2/g$, between 30 and 60 $m^2/g$, and above 60 $m^2/g$, respectively. One candidate sorbent from each group was also calcined at 1,000 °C for 1 s in the flow reactor. Each sample was analyzed for the pore size distribution produced as a result of calcination under mild conditions of 550 °C and more stringent parameters of 1,000 °C. The

results for a 25 $m^2/g$ sample of $Ca(OH)_2$ (low surface area group, below 30 $m^2/g$) are presented in Figure 7 showing the incremental pore volumes for samples produced under both conditions of calcination and sintering. For this range of surface areas, the major loss of pore volume as a result of more demanding sintering conditions occurred for pores smaller than 100 Å. Figure 8 presents the samples of intermediate surface area $Ca(OH)_2$ (52 $m^2/g$) collected after calcination at 550 and 1,000 °C in the flow reactor. Pore volume loss is evident throughout the whole pore size range from below 100 to greater than 1,000 Å. The corresponding relationship for high surface area $Ca(OH)_2$ (74 $m^2/g$) is given in Figure 9.

A high temperature inertial cascade impactor was used to collect size cuts for measurement of structural properties of calcines as a function of their particle size. The impactor was attached directly downstream of the flow reactor. Two sorbents were selected for these measurements: 16 and 36 $m^2/g$, representing low and intermediate surface area calcium hydroxides, respectively. Calcination conditions in the flow reactor were fixed at 700 °C and 1 s. The results presented in Figure 10 show the calcined surface area as a function of particle size for both sorbents. Due to the poor yield of calcine on impactor trays collecting particles of submicron size, no structural analyses were made on these fractions. For a given calcine and fixed conditions of calcination, the surface area decreases with decreasing particle size. Figure 11 presents the pore size data for the same sorbents and conditions of calcination giving median pore size as a function of particle size. Median pore size increases with decreasing particle size for a given sorbent. The data in Figures 10 and 11 indicate that sintering advances more rapidly in fine particles. As explained before, the sintering process involves the growth of necks between adjacent grains, rounding of pores at the grain boundaries, and subsequent filling of pores. With the smallest pores being filled first, the predicted behavior is for the median pore size to become larger with more advanced sintering. Surface area is therefore the earliest and most sensitive indicator of the degree of sintering.

Calcium Oxide Reactivity

Experimental values of specific surface area and porosity of calcines produced at 550 °C and 1 s in the flow reactor are shown in Figure 12. Nascent CaO with surface area as high as 78 $m^2/g$ and 0.5 porosity was formed under these mild conditions of calcination. Previous work [20] that produced sorbents with high surface area demonstrated only marginal enhancement of $SO_2$ capture by these sorbents. The theoretical effects of particle size, surface area, and porosity were explained before [4] and the existence of an optimum combination of structural properties for the reactivity of sorbent with $SO_2$ has been postulated. An effectiveness factor was used in the above work [4] to indicate the uniformity of reaction throughout the particle. An effectiveness factor of unity would indicate reaction occurring throughout the entire particle. A value significantly less than 1 would point to considerable intraparticle resistances with reaction occurring at the interface only. The modified Thiele modulus, defined here as

$$\emptyset = R\left(\frac{S^2(1-\varepsilon)}{\varepsilon^3}\right)^{1/2}$$

was used to indicate the effectiveness factor, where R = radius of CaO particle (μm), S = specific surface area of CaO ($m^2/g$), and ε = porosity of CaO (unitless). Derivation indicates that lower Ø values are associated with higher values of an effectiveness factor. Optimum performance of sorbent with $SO_2$ would therefore be expected for the CaO with a minimum Thiele modulus. The population of calcines presented in Figure 12 was approximated by the solid line in Figure 12 (numbers represent calcines representing a broad range of surface areas for further investigation). For each selected calcine, the modified Thiele modulus was calculated using the value of porosity and of specific surface area determined by the solid line in Figure 12. The value of CaO particle radius, R, was based on a Sedigraph measurement of $Ca(OH)_2$. Based on earlier research [4], no particle size change occurs during the calcination of $Ca(OH)_2$. The modified Thiele modulus, Ø, was plotted as a function of surface area and porosity in Figures 13 and 14, respectively. For the sorbents of this work, it is clear that those with intermediate surface areas (30 to 50 $m^2/g$) and porosities (0.25 to 0.35) would have the lowest Thiele moduli.

These calculations were verified in the STDR operated at 550 °C with 5 vol percent $O_2$, 3,000 ppm $SO_2$, and the balance $N_2$. Five sorbents with dissimilar structural properties were used for the investigation of the effect of Thiele modulus. The $Ca(OH)_2$ sorbents that had produced CaO upon calcination in the flow reactor (550 °C and 1 s) having surface areas varying from 6 to 78 $m^2/g$ and porosities varying from 0.11 to 0.5 were used for reactivity study in the STDR. The range of contact time from 0.3 to 5 s was investigated for each sorbent. The data were reduced and the reactivities obtained for 2 s contact time were used for the comparison. Theoretical predictions based on Thiele modulus indicated that sorbent no. 17 should reveal the highest reactivity with $SO_2$. For this sorbent, the Thiele modulus reached an experimental minimum suggesting a high effectiveness factor. Temperature and concentration conditions in the interior are similar to those at the exterior. The results of STDR reactivity testing at 550 °C for 2 s are presented in Figure 15. Conversion in the STDR is plotted as a function of the Thiele modulus of sorbents produced during calcination at the same temperature in the flow reactor operated without $SO_2$. The maximum conversion for the five sorbents investigated was measured for $Ca(OH)_2$ sorbent no. 17, which upon calcination in the flow reactor revealed CaO with a calculated Thiele modulus of 320. Consistent with the prediction by Thiele modulus analysis, the conversion was somewhat lower for $Ca(OH)_2$ sorbents with specific surface area above 50 $m^2/g$ and porosity above 0.4. For CaO produced from these sorbents, the diffusion rates were probably considerably lower as a result of larger particle size and surface area.

## CONCLUSIONS

The following conclusions can be drawn from the results of this study:

1. Sorbents having high surface area and porosity can be produced using a mixture of methyl alcohol and water for hydration of CaO in the "double hydration method." There was good correlation between surface area and porosity of $Ca(OH)_2$ sorbents produced from one precursor limestone.

2. For mild conditions of sintering in the flow reactor, correlation could be found between structural properties of $Ca(OH)_2$ and nascent CaO. Since an early stage of sintering was simulated, the correlation was closer for porosity than for surface area. For sorbents produced from one precursor limestone and calcined under fixed conditions in the flow reactor, calcination of higher surface area/porosity $Ca(OH)_2$ resulted in higher surface area/porosity of CaO. Calcines produced from the intermediate surface area (30 to 60 $m^2/g$) $Ca(OH)_2$ had lower porosities and surface areas due to fewer pores in the range from 100 to 1,000 Å.

3. Structural properties of calcines were measured as a function of particle sizes. The surface area decreased and median pore size increased with decreasing particle size in the 1.2 to 7.5 µm size range (for a given calcine and fixed conditions of calcination).

4. Reactivity of $Ca(OH)_2$ ranging from 6 to 74 $m^2/g$ was tested in a short time differential reactor operated at constant sulfation conditions. Optimum surface area and porosity of CaO was determined theoretically and verified experimentally. The maximum conversion with $SO_2$ among sorbents tested was measured for an intermediate $Ca(OH)_2$ sorbent with 39 $m^2/g$ surface area and 0.23 porosity. $Ca(OH)_2$ sorbents with surface areas above 50 $m^2/g$ revealed somewhat lower conversion, probably due to a decreased diffusion rate. Thus, the highest surface area sorbents did not display the best reactivity with $SO_2$ as had been expected originally.

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## REFERENCES

1. Borgwardt, R.H., and K.R. Bruce, "EPA Study of Hydroxide Reactivity in a Differential Reactor," *Proc. 1986 Joint Symp. Dry $SO_2$ and Simul. $SO_2/NO_x$ Control Technol. 1*, EPA-600/9-86-029a (NTIS PB87-120465), p. 15-1 (Oct., 1986).

2. Cole, J.A., J.C. Kramlich, W.R. Seeker, G.D. Silcox, G.H. Newton, D.J. Harrison, and D.W. Pershing, "Fundamental Studies of Sorbent Reactivity in Isothermal Reactors," *Proc. 1986 Joint Symp. Dry $SO_2$ and Simul. $SO_2/NO_x$ Control Technol. 1*, EPA-600/9-86-029a (NTIS PB87-120465), 16-1 (Oct., 1986).

3. Gullett, B.K., and J.C. Kramlich, "Fundamental Processes Involved in $SO_2$ Capture by Calcium-Based Adsorbents," *Proc. 4th Ann. Pitts. Coal Conf.* (Sept.-Oct., 1987).

4. Gullett, B.K., and J.A. Blom, "Calcium Hydroxide and Calcium Carbonate Particle Size Effects on Reactivity with Sulfur Dioxide," *React. Solids*, 3, 337, 1987.

5. Harrison, D.J., G.H. Newton, and D.W. Pershing, "Calcination of Calcium-Based Sorbents for Control of $SO_2$ Emissions from Coal-Fired Boilers," *Western States Sect., Combust. Inst. Fall Meet.*, Davis, CA (Oct., 1985).

6. Newton, G.H., D.J. Harrison, G.D. Silcox, and D.W. Pershing, "Control of $SO_x$ Emissions by In-Furnace Sorbent Injection: Carbonates vs. Hydrates," *AIChE Ann. Meet.*, Chicago (Nov., 1985).

7. Slaughter, D.M., G.D. Silcox, P.M. Lemieux, G.H. Newton, and D.W. Pershing, "Bench-Scale Evaluation of Sulfur Sorbent Reactions," *Proc. 1st Joint Symp. Dry $SO_2$ and Simul. $SO_2/NO_x$ Control Technol. 1*, EPA-600/9-85-020a (NTIS PB85-232353), 11-1 (July, 1985).

8. Borgwardt, R.H., and K.R. Bruce, "Effect of Specific Surface Area on the Reactivity of CaO with $SO_2$," *AIChE J.*, 32, 239 (1986).

9. Hartman, M., J. Pata, and R.W. Coughlin, "Influence of Porosity of Calcium Carbonates on Their Reactivity with Sulfur Dioxide," *Ind. Eng. Chem. Process Des. Dev.*, 17, 411 (1978).

10. Simons, G.A., "Parameters Limiting Sulfation by CaO," *AIChE J.*, 34, 167, (1988).

11. Gullett, B.K., J.A. Blom, and R.T. Cunningham, "Porosity, Surface Area, and Particle Size Effects of CaO Reacting with $SO_2$ at 1,100 °C," *React. Solids*, 6, 263, 1988.

12. Borgwardt, R.H., "Sintering of Nascent Calcium Oxide," *Chem. Eng. Sci.*, 44, 53, 1989.

13. Borgwardt, R.H., "Calcium Oxide Sintering in Atmospheres Containing Water and Carbon Dioxide," *Ind. Eng. Chem. Res.*, 28, 493, 1989.

14. Gullett, B.K., and K.R. Bruce, "Pore Distribution Changes of Calcium-Based Sorbents Reacting with Sulfur Dioxide," *AIChE J.*, 33, 1719, 1987.

15. Kirchgessner, D.A., and W. Jozewicz, "Structural Changes in Surfactant-Modified Sorbents During Furnace Injection," *AIChE J.*, 35, 500, 1989.

16. Kirchgessner, D.A., and W. Jozewicz, "Enhancement of Reactivity in Surfactant-Modified Sorbents for Sulfur Dioxide Control," *Ind. Eng. Chem. Res.*, 28, 413, 1989.

17. Kirchgessner, D.A., and W. Jozewicz, "Laboratory and Commercial-Scale Results of Testing Surfactant-Modified Sorbent," *Proc. First Comb. FGD and Dry $SO_2$ Control Symp.*, Vol. 2, EPA-600/9-89-036b (NTIS PB89-172167), 5-121, 1989.

18. Jozewicz, W., and D.A. Kirchgessner, "Activation and Reactivity of Novel Calcium-Based Sorbents for Dry $SO_2$ Control in Boilers," *Powder Technol.*, 58, 221, 1989.

19. Jozewicz, W., and D.A. Kirchgessner, "Calcination of Calcium Hydroxide Sorbent in the Presence of $SO_2$ and its Effect on Reactivity," presented at the Spring National Meeting of AIChE, Houston, TX, April 1989.

20. Gooch, J.P., E.B. Dismukes, R. Beittel, J.L. Thompson, and S.L. Rakes, Proceedings: 1986 Joint Symposium on Dry $SO_2$ and Simultaneous $SO_2/NO_x$ Control Technologies, Vol. 1, U.S. Environmental Protection Agency, Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, EPA-600/9-86-029a (NTIS PB87-120465), 1986, p. 11-1.

21. Lovell, W.G., V.A. Miller, M.J. Mulligan, and H.K. Lichtenwalner, "Especially Reactive Lime and Method of Producing It," U.S. Patent No. 2,474,207, July 1945.

22. Gullett, B.K., K.R. Bruce, and R.M. Machilek, "Apparatus for Short Time Measurements in a Fixed Bed, Gas/Solid Reactor," accepted for publication in *Rev. Sci. Instr.*

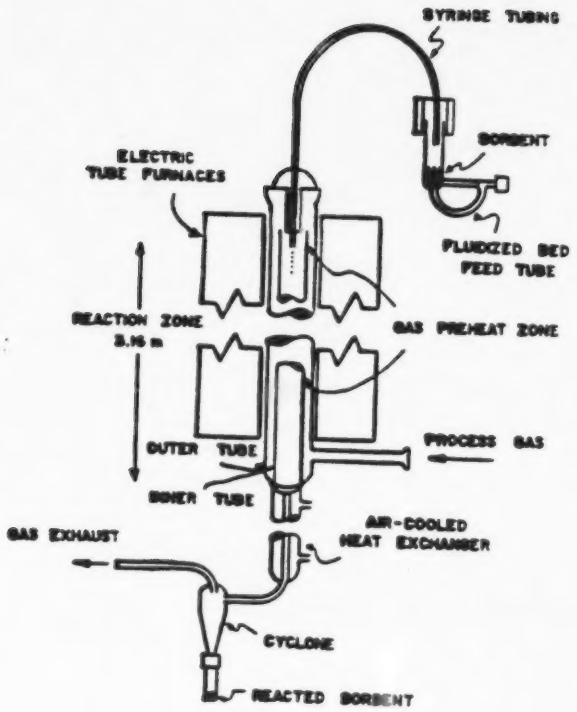


Figure 1. Isothermal flow reactor.

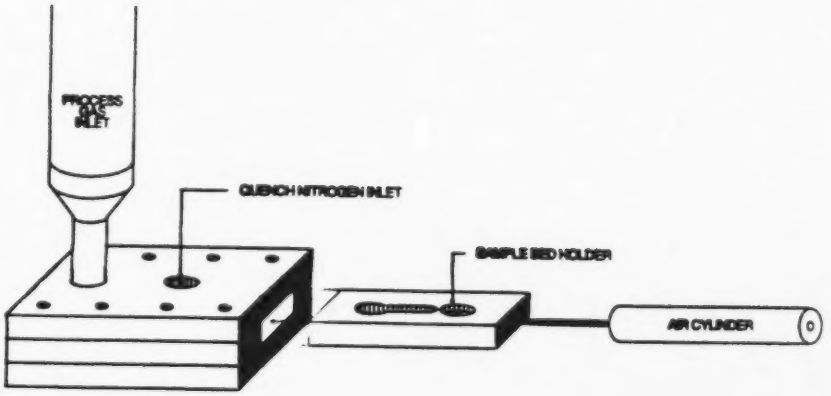


Figure 2. Short time differential flow reactor.

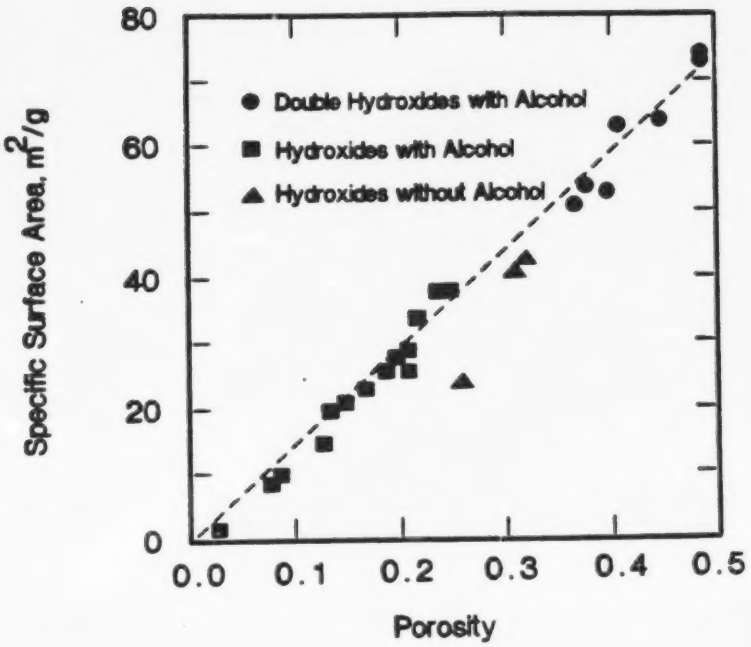


Figure 3. Population of calcium hydroxide sorbents used for this study (Longview $CaCO_3$ precursor used).

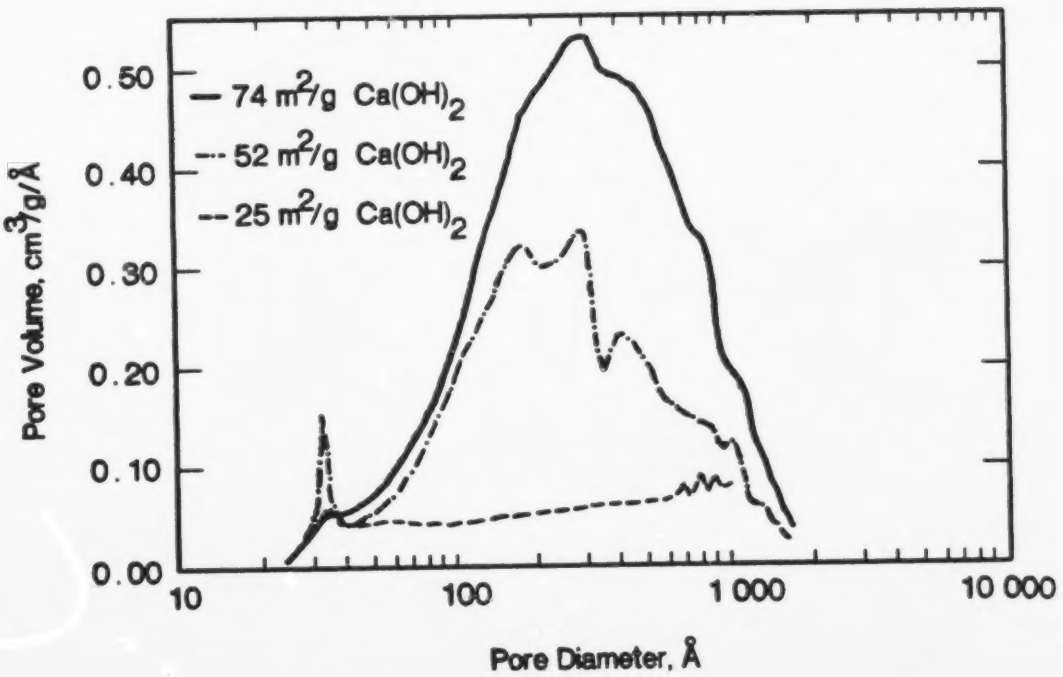


Figure 4. Changes in pore size distribution for calcium hydroxide sorbents of varying surface area and porosity.

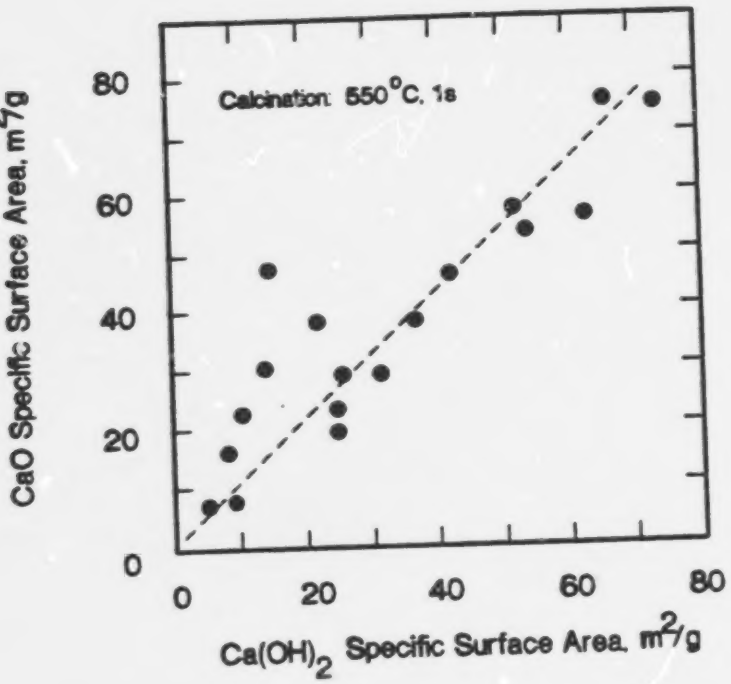


Figure 5. Correlation between surface area of calcium hydroxide and nascent calcium oxide (constant calcination conditions of 550 °C and 1 s).

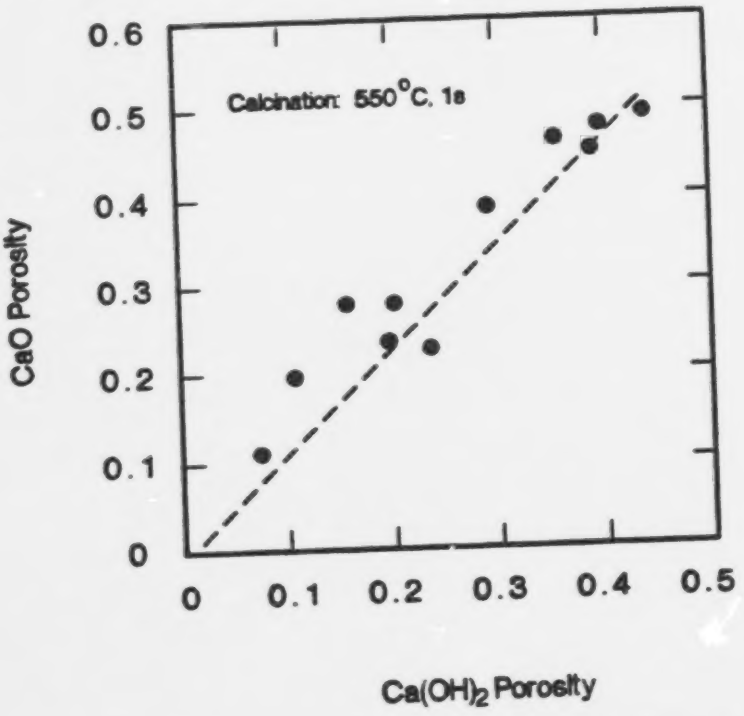


Figure 6. Correlation between porosity of calcium hydroxide and nascent calcium oxide (constant calcination conditions of 550 °C and 1 s).

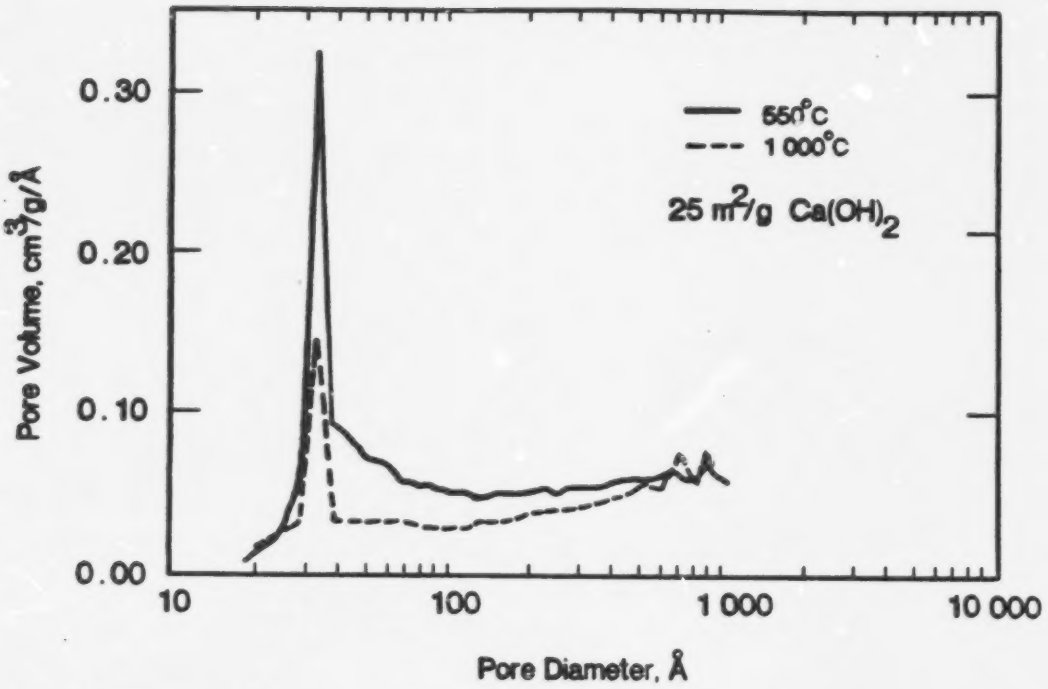


Figure 7. Pore size distribution changes resulting from calcination and sintering of low surface area calcium hydroxide.

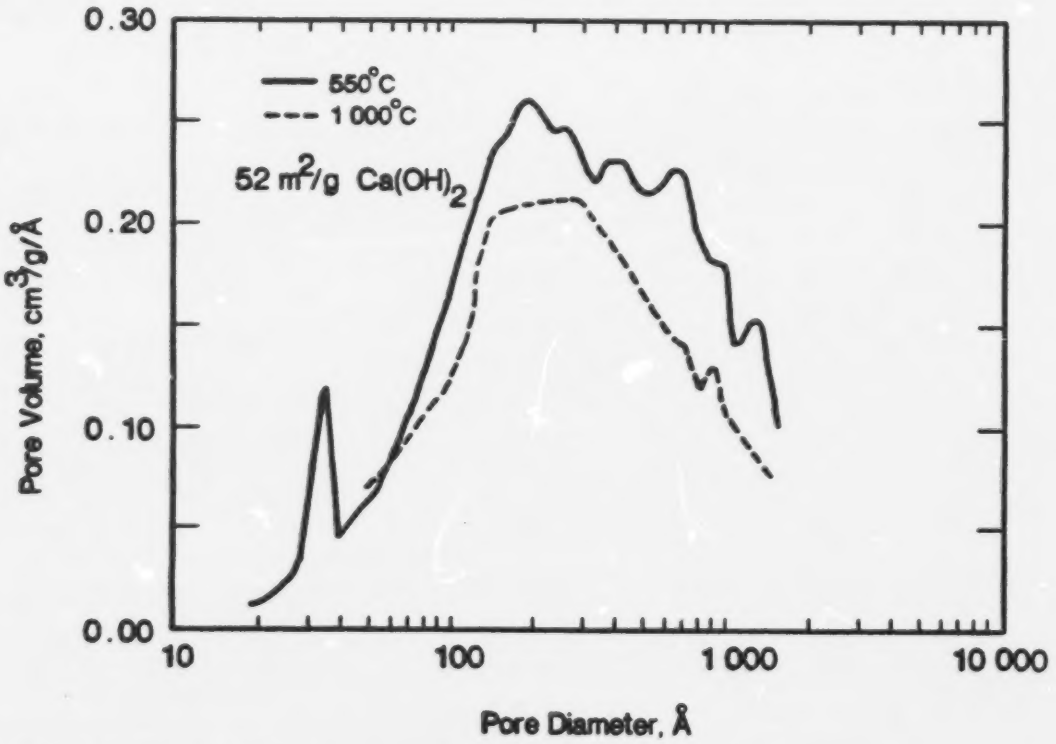


Figure 8. Pore size distribution changes resulting from calcination and sintering of intermediate surface area calcium hydroxide.

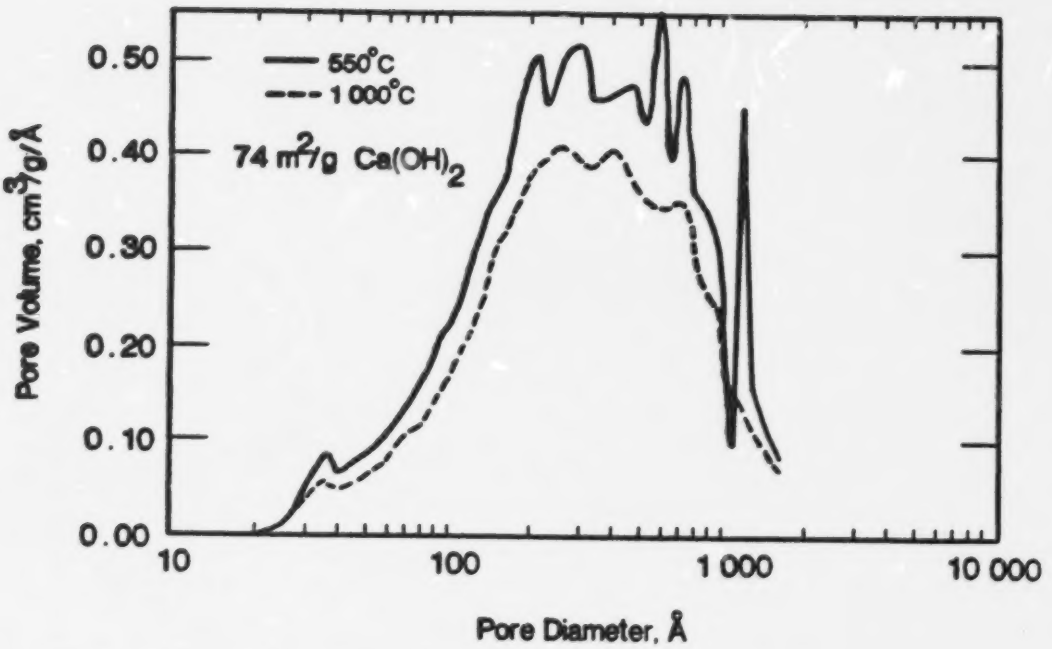


Figure 9. Pore size distribution changes resulting from calcination and sintering of high surface area calcium hydroxide.

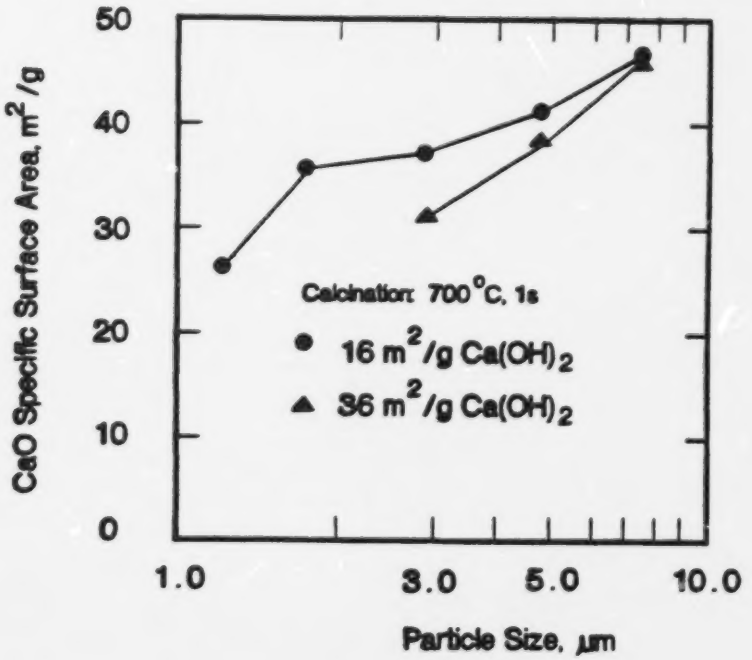


Figure 10. Calcined surface area as a function of particle size for two different sorbents (fixed calcination conditions 700 °C, 1 s).

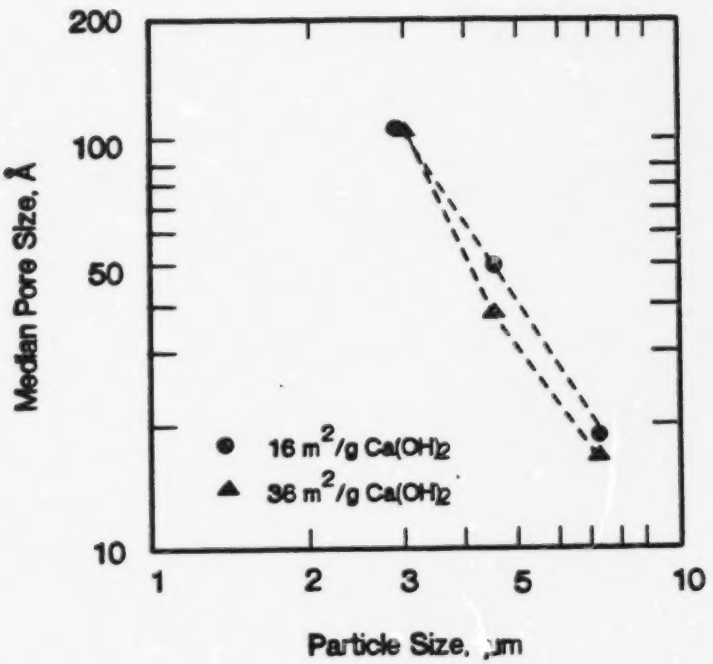


Figure 11. Median pore size as a function of particle size for two different sorbents (fixed calcination conditions 700 °C, 1 s).

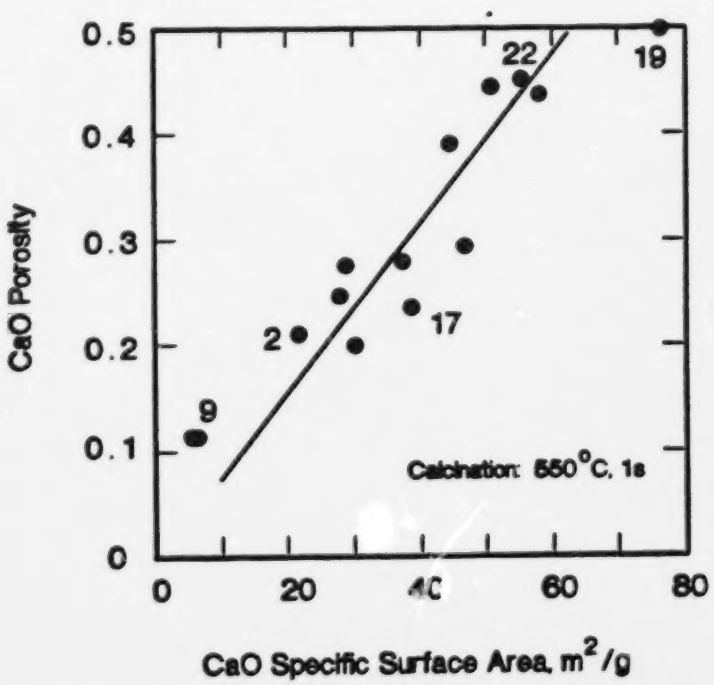


Figure 12. Experimental values of surface area and porosity of calcines produced in the flow reactor (550 °C, 1 s).

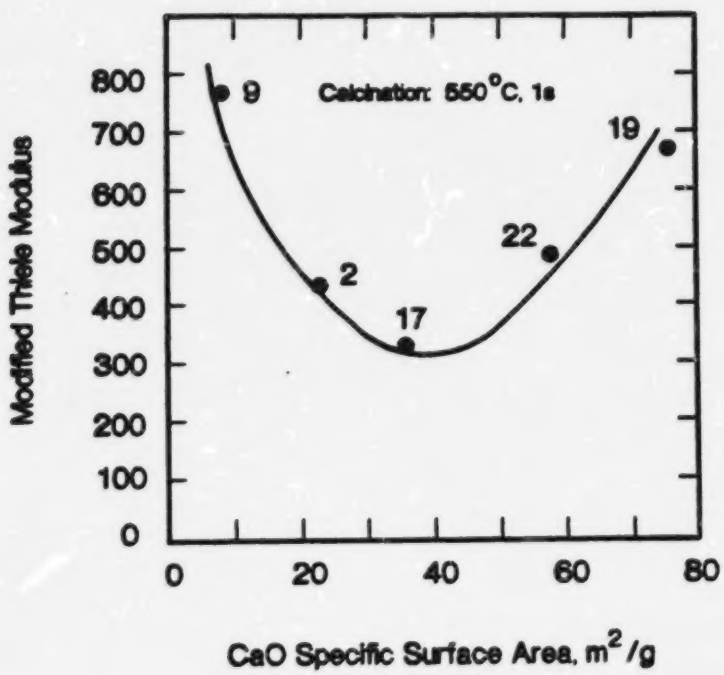


Figure 13. Modified Thiele modulus, Ø, as a function of surface area.

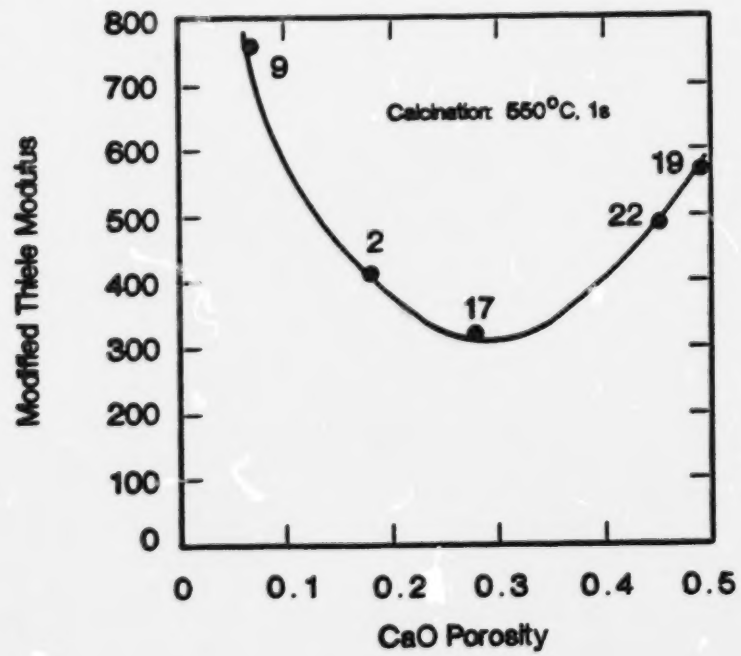


Figure 14. Modified Thiele modulus, Ø, as a function of porosity.

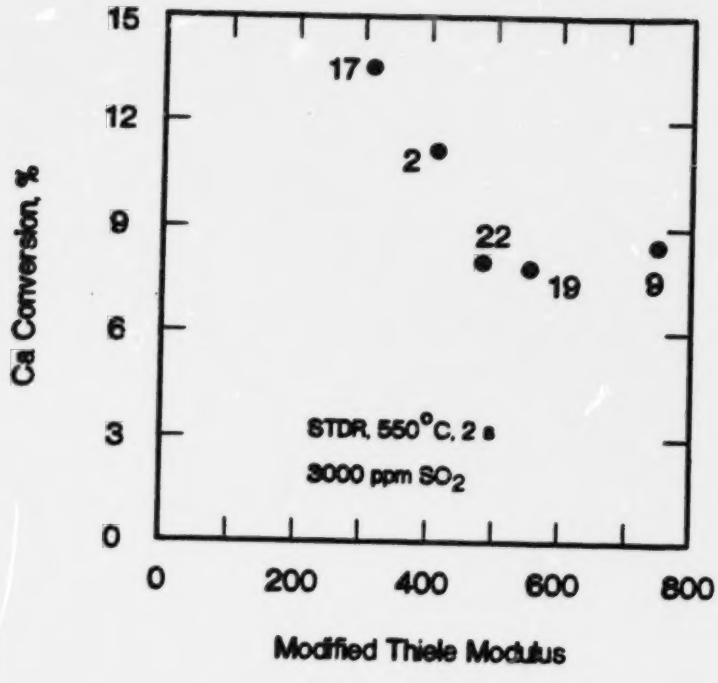


Figure 15. Calcium conversion as a function of modified Thiele modulus (STDR, 550 °C, 2 s, 3,000 ppm $SO_2$).